

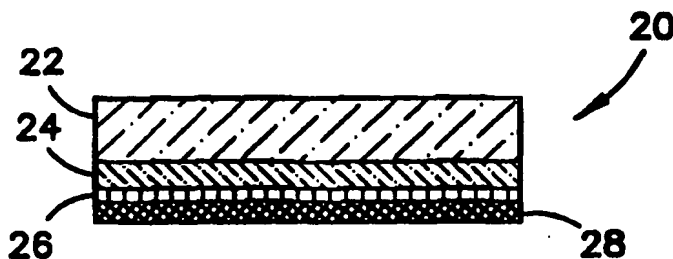
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(21) International Application Number: PCT/US97/23689 (22) International Filing Date: 19 December 1997 (19.12.97) (30) Priority Data: 08/791,075 29 January 1997 (29.01.97) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/791,075 (CIP) Filed on Not furnished (71) Applicant (for all designated States except US): TETRA LAVAL HOLDINGS & FINANCE S.A. [CH/CH]; Avenue Général Guisan 70, CH-1009 Pully (CH). (72) Inventor; and (75) Inventor/Applicant (for US only): FRISK, Peter [SE/US]; 2300 Lincoln Park West, Chicago, IL 60614 (US). (74) Agent: CATANIA, Michael, A.; Tetra Pak, U.S. Intellectual Property Dept., 909 Asbury Drive, Buffalo Grove, IL 60089 (US).			(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published Without international search report and to be republished upon receipt of that report.
(54) Title: TRANSPARENT HIGH BARRIER MULTILAYER STRUCTURE			
(57) Abstract <p>A transparent multilayer structure (20, 21, 31, 31') is disclosed which may be used as a flexible self-supporting container (30) for a flowable food product such as fruit juice, cheese, milk, tomato juice, soup and the like. The transparent multilayer structure (20, 21, 31) possesses superior barrier properties to oxygen, water vapor and aromatic gases. The multilayer structure (20, 21, 31) may include an exterior layer (22, 22') having a metal oxide deposition (24, 24') laminated to an interior layer (28, 28') through use of an adhesive (26). In one embodiment, the metal oxide (24, 24') is SiO<sub>x</sub> where x has a value between 1.5 and 2.2 thereby allowing for a transparent multilayer structure (20, 21, 31). The metal oxide (24, 24') may be deposited on the exterior layer (22, 22') through a number of various methods. An exemplary method is plasma-enhanced chemical vapor deposition. The exterior layer (22, 22') may be biaxially oriented PET and an interior layer (28, 28') may be a blend of LLDPE and LDPE. A barrier layer (27, 27') and a polyolefin layer (29, 29') may also be included in the transparent multilayer structure (20, 21, 31). The barrier layer (27, 27') may be EVOH, PEN, liquid crystal polymers or the like.</p>			



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## Title

## TRANSPARENT HIGH BARRIER MULTILAYER STRUCTURE

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## Technical Field

The present invention relates to transparent high barrier multilayer structures. Specifically, the present invention relates to a transparent high barrier pouch composed of a multilayer film structure having at least one layer of a polymer with a metal oxide deposition thereon.

10

## Background Art

High barrier flexible materials for packaging strive for glass-like properties without the weight associated with glass containers. Many inventions have been developed which attempt to reach this "Holy Grail" of the packaging industry. For example, Löfgren *et al*, U.S. Patent No. 5,122,410, for a Laminated Packing Material With Gas and Aroma Barrier Properties discloses a laminate of two thermoplastic layers, each coated with a silicon compound, bonded together by an intermediate layer of an adhesive agent. The silicon compound may be SiO<sub>2</sub> which provides good gas and aroma barrier properties for packages fabricated from the laminate.

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20

Deak *et al*, U.S. Patent No. 5,085,904 for Barrier Materials Useful For Packaging discloses a multilayer structure of a 10-75 nanometer thick layer of SiO vacuum deposited on a resin substrate of either polyester or polyamide with at least a 20 nanometer thick layer of SiO<sub>2</sub> vacuum deposited on the SiO layer. Deak *et al* specifically teaches "the necessity of the SiO/ SiO<sub>2</sub> multilayer combination in terms of barrier properties." Deak *et al* further teaches that "it is

25

essential that some thickness of SiO layer be present, since it is the combination of resin substrate and the SiO and SiO<sub>2</sub> layers that provides the desirable barrier properties." Deak *et al* also teaches that the use of SiO will impart a yellow coloration which may not be perceptible if the SiO layer is very thin. However, at  
5 these small thickness the SiO layer provides virtually no barrier properties unless combined with a SiO<sub>2</sub> layer. Deak *et al* also teaches that the use of SiO<sub>2</sub> alone is limited due to decreasing flexibility with increasing thickness. Thus, according to Deak *et al*, only a multilayer structure of a 10-75 nanometer thick layer of SiO vacuum deposited on a resin substrate of either polyester or polyamide with at  
10 least a 20 nanometer thick layer of SiO<sub>2</sub> vacuum deposited on the SiO layer will exhibit sufficient barrier properties with an acceptable flexibility.

The foregoing patents, although efficacious in the protection of their contents, are not the denouement of the problems of the packaging industry. There are still unresolved problems which compel the enlargement of inventions  
15 in the packaging industry.

## 3

## Disclosure of the Invention

The present invention is the next step toward a glass-like flexible material.

The transparency of the flexible material allows one to view the contents of the  
5 packaging while the high barrier properties virtually prevent the ingress of gases  
into the packaging.

One aspect of the present invention is a transparent multilayer structure.  
The structure is composed of an exterior film, a metal oxide deposited on the  
exterior film and an interior film. The exterior film is selected from the group  
10 consisting of high density polyethylene ("HDPE"), polypropylene ("PP"),  
polyethylene naphthalate ("PEN"), polyethylene terephthalate ("PET") and  
polyamide ("PA"). The exterior film may be unoriented, mono-oriented or  
biaxially oriented. The metal oxide deposition on the exterior film has a thickness  
range of approximately 5 to 500 nanometers and has a formula of  $MO_x$  where x  
15 has a range of approximately 1.5 to approximately 2.5. M is selected from the  
group consisting of silicon, aluminum and iron. The interior film is juxtaposed to  
the metal oxide deposition.

The exterior film may also be a print layer. The structure may have a  
signage printed on the metal oxide deposition. The exterior film may have a  
20 thickness range of approximately 8 to approximately 20 microns. The interior  
film may have a thickness range of approximately 25 to approximately 150  
microns. The interior film may be laminated to the exterior film and metal oxide

deposition through utilization of an adhesive. The structure may be a container for flowable materials. The structure may be a laminate. The metal oxide deposition is deposited onto the exterior film through a process selected from the group consisting of plasma-enhanced chemical vapor deposition, metalorganic chemical vapor deposition, halide transport chemical vapor deposition, liquid atmospheric photo chemical deposition, electron beam evaporation, pulsed laser ablation, atomic layer epitaxy, ion implantation, molecular beam epitaxy and RF magnetron sputtering.

The interior film may be selected from the group consisting of linear low density polyethylene ("LLDPE"), ultra low density polyethylene, metallocene linear low density polyethylene, low density polyethylene ("LDPE"), medium density polyethylene ("MDPE"), HDPE, PP, copolymers of polypropylene, copolymers of ethylene vinyl acetate and mixtures thereof.

Another aspect of the present invention is a film structure that builds upon the previously mentioned film structure. This second film structure has a barrier layer bonded to the interior film layer and a polyolefin layer bonded to the barrier layer. A preferred barrier layer is composed of an ethylene vinyl alcohol ("EVOH"). The polyolefin layer is preferably a blend of LLDPE and a LDPE.

Another aspect of the present invention is a process for fabricating a transparent multilayer structure. The first step of the process is to provide an exterior film selected from the group consisting of PET, PP, PA, PEN and HDPE,

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with a metal oxide deposition thereon. The next step is laminating the interior film to the exterior film.

Another aspect of the present invention is a self-supporting transparent container for flowable materials. The self-supporting transparent container is  
5 fabricated from the basic film structure or the more extensive film structure which were mentioned above.

The self-supporting transparent container may also include a transverse seal having an unsealed area of a predetermined configuration. The transverse seal may have a tear notch for exposing the unsealed area while partially  
10 maintaining the transverse seal. The exposed unsealed area permits the placement of an insert for removing the contents of the self-supporting transparent container. The insert corresponds in shape to the predetermined configuration of the unsealed area. The insert may have an elongated body with an aperture therethrough. The elongate body has an insert portion for penetration to the  
15 contents, a breaking portion, a spout portion, and a knob.

## 6

## Brief Description of Several Views of the Drawings

There is illustrated in FIG. 1 a cross-sectional view of one embodiment of a laminate of the present invention.

There is illustrated in FIGS. 1A-1C cross-sectional views of other.  
5       embodiments of a laminate of the present invention.

There is illustrated in FIG. 2 a perspective view of a self-supporting transparent container of the present invention.

There is illustrated in FIG. 3 a perspective view of an insert placed within a self-supporting transparent container of the present invention.

10       There is illustrated in FIG. 4 a partial view of a self-supporting transparent container of the present invention with an unsealed area.

There is illustrated in FIG. 5 a side view of an insert utilized in conjunction with a self-supporting transparent container of the present invention.

15       There is illustrated in FIG. 6 a side view of an insert utilized in conjunction with a self-supporting transparent container of the present invention.

There is illustrated in FIG. 7 a graph of the Gelbo Flex testing of three flexible barrier materials of the present invention.

There is illustrated in FIG. 8 a graph of the oxygen permeation versus humidity for PET/SiOx compared to EVOH.

20       There is illustrated in FIG. 9 a graph of oxygen permeation versus PET/MOx film elongation for three flexible barrier materials of the present invention.

There is illustrated in FIG. 10 a graph of oxygen permeation versus temperature for PET/SiOx compared to PVDC.



### Best Modes For Carrying Out The Invention

The packaging of liquid food products such as fruit juices has assumed various forms for aesthetic and functional purposes. Packaging should be non-scalping so as not to impoverish the contents of its aromatic flavorings and essential oils. Packaging should be a barrier to gases such as oxygen to prevent oxidation of the contents, and an aroma barrier. Packaging should also be durable to withstand distribution from a packaging site to a retail site. Packaging should also be pleasing to the consumer in order to entice the consumer to purchase the product.

10 One age-old method of aesthetic packaging is the transparent glass bottle which allows the consumer to view the contents prior to purchase. In this manner, the consumer may verify that the contents are not contaminated and have not degraded to an unacceptable by-product. However, the weight of a glass bottle is unacceptable for today's packaging needs. The transparent multilayer structure  
15 of the present invention provides many of the barrier, durability and aesthetic properties of the glass bottle without the unnecessary weight. The novel transparent multilayer structure of the present invention provides almost crystal clear transmission of light while maintaining the barrier and durability properties necessary for today's packaging.

20 As shown in FIG. 1, the laminate 20 is generally composed of an exterior film.22, a metal deposition 24, an adhesive 26 and an interior film.28. The laminate 20 is transparent, durable and a barrier to various gases including oxygen.

The exterior film.22 may be selected from HDPE, PEN, PA, PP and PET.

25 The exterior film may be unoriented, mono-oriented or biaxially oriented. The

metal deposition 24 may have the formula  $MO_x$  where x has a range of approximately 1.5 to approximately 2.5. M may be silicon, aluminum or iron, with a preference for silicon. The interior film 28 may be selected from the group consisting of linear low density polyethylene, ultra low density polyethylene, 5 metallocene linear low density polyethylene, low density polyethylene, medium density polyethylene, high density polyethylene, polypropylene, copolymers of polypropylene, copolymers of ethylene vinyl acetate and mixtures thereof.

Various adhesives are suitable as the adhesive layer 26 for joining the interior film 28 to the exterior film 22 and metal deposition 24. For example, a 10 solvent-based adhesive available from Novacote and a solvent free adhesive from Novacote may be used in the present invention. A modified ethylene copolymer or a polyurethane adhesive may be used for this purpose. One polyurethane adhesive suitable for such use is sold by Novacote International of Hamburg, Germany. A modified ethylene copolymer is BYNEL CXA sold by DuPont.

15 The exterior film 22 may have a thickness range of approximately 8 to 20 microns. The interior film 28 may have a thickness of approximately 25 to 150 microns. The metal oxide deposition 24 may have a thickness range of approximately 5 to 500 nanometers. The stoichiometry of the metal oxide is important to maintain the transparency and the high barrier properties of the 20 multilayer structure 20. In the formula  $MO_x$  where M is either aluminum, silicon or iron, and x is between 1.8 and 2.5, the ability to deposit the metal oxide within this stoichiometric range prevents the multilayer structure from becoming tinged thereby losing its transparency. For example, when M is silicon and x is near 1.0, the multilayer structure will have a yellow tinge indicative of silicon oxide, a 25 semiconductor which has a relatively narrow electron band gap between a filled

valence band and an empty conduction band thereby allowing for the absorption of light. Whereas when M is silicon and x is near 2, the metal deposition is silicon dioxide, an insulator which has a relatively large electron band gap between a filled valence band and an empty conduction band thereby allowing for the transmission of light. Thus, it is very important that the deposition of the metal oxide be performed in a manner that will ensure this stoichiometric range in order to have the transparency as well as the expected barrier properties as further illustrated in the graphs at FIGS. 7-10.

The metal oxide deposition 24 may be deposited on the exterior film 22 through a number of deposition methods. These methods include plasma-enhanced chemical vapor deposition, metalorganic chemical vapor deposition, halide transport chemical vapor deposition, liquid atmospheric photo chemical deposition, electron beam evaporation, pulsed laser ablation, atomic layer epitaxy, ion implantation, molecular beam epitaxy and RF magnetron sputtering. A preferred deposition method is plasma enhanced chemical vapor deposition described in Fayet *et al*, U.S. Patent No. 5,531,060 which is hereby incorporated by reference.

Referring still to FIG. 1, a preferred embodiment of the laminate 20 may have the exterior film 22 composed of a biaxially oriented PET with a silicon oxide deposition 24 having the following stoichiometry,  $\text{SiO}_x$ , where x has value between 1.5 and 2.5. In this preferred embodiment, the interior film 28 is composed of a blend of LLDPE and LDPE.

As shown in FIG. 1A, a more extensive multilayer film structure 21 is disclosed which incorporates the film structure/laminate 20 of FIG. 1. Film structure 21 has an exterior film layer 22' with a metal deposition 24' thereon, an

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interior film layer 28', a barrier layer 27 and a polyolefin layer 29. The interior film layer 28' may be a misnomer since it is no longer an interior layer but a core layer. Adhesive layers 26A, 26B and 26C bond the other layers together.

A preferred barrier layer is composed of EVOH or EVOH and a blend of a  
5 compatible polymer. Other polymers which may be used as a barrier layer include but are not limited to polyvinyl dichloride ("PVDC"), PEN, MXD6 polyamide, PAN, liquid crystal polymers, and the like. A preferred polyolefin layer is a blend of LLDPE and LDPE.

The thickness of the film structure 21 may vary depending on the  
10 application. In one embodiment, the film structure 21 may have an exterior film layer 22' with the metal oxide 24' thereon in a thickness range of 6-20 microns (preferably 8 to 12 microns), the interior film layer 26' in a thickness range of 5-30 microns, the barrier layer 27 in a thickness range of 1-15 microns, the polyolefin layer 29 in a thickness range of 5-50 microns, and the adhesive layers  
15 26A-C in a thickness range of 1-5 microns.

Yet another variation on the film structure is set forth in FIG. 1B. The film structure 31 has an exterior film layer 22' with a metal oxide 24' thereon, a barrier layer 27' and a polyolefin layer 29'. A variation on this film structure 31', shown in FIG. 1C, would have the exterior film layer 22' with a metal oxide 24'  
20 thereon, polyolefin layer 29' and a barrier layer 27' as the interior layer in contact with the product. There are also adhesive layers 26D and 26E. The barrier layer 27' and the polyolefin layer 29' are the same as described in FIG. 1A. The polyolefin layers 29 and 29' may be composed of materials as described for interior layer 28 in reference to FIG. 1. Also, the adhesive layers 26A-E may be  
25 as described above in reference to FIG. 1.

As shown in FIG. 2, the container 30 has an upper transverse seal 32, a longitudinal seal 34, a first oblique seal 36 and a second oblique seal 38 and a bottom seal 40. The interior 42 of the container 30 contains a flowable material such as a pumpable food. One particular use of the container 30 is for juices.

5       The container 30 is transparent except for any signage 44 which may be added to indicate the contents or source of the contents. The signage 44 may be created by reverse printing on the metal deposition 24 of the laminate 20. Also, Flexo, Roto and Offset printing methods may be employed. However, those skilled in the art will recognize that other printing methods may be employed  
10       without departing from the scope or spirit of the present invention. The signage 44 may be placed at any desired position on the container 30 and may be of any size or shape. The self-supporting transparent container 30 may be fabricated on a vertical form, fill and seal machine.

      The insert 50 is placed through the top of the container 30 to reach the  
15       contents in the interior 42. The insert 50 is positioned through an opening in the container 30, explained below, in a manner which forms a liquid tight seal thereby preventing spillage of the contents of the container 30.

      As shown in FIG. 4, the transverse seal 32 has an unsealed area 64 for placement of the insert 50 therethrough. The transverse seal 32 also has a tear  
20       notch 66 for partially tearing open the seal to reveal the unsealed area 64. When in use, the transverse seal 32 close to the notch 66 is first torn by the consumer. This tear propagates into the unsealed area 64 which now forms an opening into the package. The unsealed area 64 has a larger diameter at the top which decreases as the unsealed area 64 approaches the contents portion of the container  
25       30. The diameter at the bottom of the unsealed area 64 may be designated D1.

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The insert 50 may be positioned into the opening/unsealed area 64 to access the contents of the package. A specially designed heat sealing bar, not shown, fabricates the transverse seal 32 having the unsealed area 64.

As shown in FIG. 5, one aspect of the straw insert 50 has an elongate body 52, an aperture 54 therethrough, an insert portion 56, a spout portion 57, a breaking portion 58, and a knob 60. The insert portion 56 is inserted through the tear opening. To secure a liquid tight insert, the outside diameter of the insert portion 56, designated D2, should be  $D2 \leq 2(D1/3.14)$ . The diameter of the top part of the insert portion 56 is gradually increasing to provide a "natural stop."

5 The spout portion 57 has a fairly constant diameter. The spout portion 57 protrudes from the container 30 and allows for pouring or drinking of the contents. The breaking portion 58 is broken to allow pouring or drinking of the contents from the spout portion 57. The knob 60 is above the breaking portion 58. The knob 60 may be gripped by a consumer and twisted, thereby breaking

10 the insert 50 at the breaking portion 58 and allowing for removal of the knob 60. Removal of the knob 60 may allow for the pouring and drinking of the contents. As shown in FIG. 6, the knob 60 may then be placed within the spout portion 57 to reseal the container 30 thereby eliminating leakage of the contents.

The present invention will be described in the following examples which

20 will further demonstrated the efficacy of the novel multilayer transparent structure, however, the scope of the present invention is not to be limited by these examples.

TABLE ONE

	<u>Layer.:</u>	<u>Comment:</u>	<u>Type:</u>
5	PET	Suitable for Food Packaging Material	48 Gauge Biaxially Oriented PET
	SiOx	Suitable for Food Packaging Material	Plasma Enhanced Chemical Vapor Deposited SiOx
10	Printing Ink	Suitable for Food Packaging Material	Flexo , Max 8 colors Roto
15	Adhesive	Food Grade Adhesive	Adhesive for laminating LDPE film to SiOx surface Retort/Hot Fill specification
20	LDPE/LLDPE LLDPE/LDPE Polymers	Food Grade	3.5 Mil thick blown film of blend: 75% LDPE , MFI: 0.7-0.8 25% C4 - LLDPE: MFI 0.8-1.0

Table One sets forth the specifications for one film structure of a flexible barrier material of the present invention which is described in Examples One through Six. The flexible barrier material has one heat sealable side for fabrication into a stand-up pouch. The flexible barrier material is transparent, has a high barrier, and is a laminate with reverse printed 48 Gauge PET/SiOx film, suitable for tear opening or straw insert. Examples One through Six demonstrate the novel properties of the flexible barrier material of the present invention.

TABLE TWO

5	ENGLISH		METRIC (SI)		
	PROPERTY	TEST	UNITS	VALUE	UNITS
	VALUE				
10	GAUGE	ASTM D374	micron	105	Mil 4.2



## EXAMPLE ONE

5	TABLE THREE				
	METRIC (SI)				
	ENGLISH	PROPERTY TEST	UNITS	VALUE	UNITS
10	VALUE				
	WATER	ASTM F1249	gm/m <sup>2</sup> 24h	0.61	gm/100in <sup>2</sup> /24h 0.039
	VAPOR				
15	TRANSMISSION				

ASTM F1249 is a test for determining the rate of water vapor transmission through flexible barrier materials. The water vapor transmission rate is defined as the time rate of water vapor flow normal to the surfaces, under steady-state conditions, per unit area.

The test is conducted in a diffusion cell composed of a dry chamber and a wet chamber separated by the flexible barrier material to be tested. The diffusion cell is placed in a test station where the dry chamber and the top of the film are swept with dry air. Water vapor diffusing through the film mixes with the air and is carried into a pressure-modulated infrared sensor. This sensor measures the fraction of infrared energy absorbed by the water vapor and produces an electrical signal, the amplitude of which is proportional to water vapor concentration. This amplitude is compared to the amplitude of a calibration film for calculation of the transmission rate of the barrier material. The water vapor transmission test

provides valuable information directly related to shelf life and packaged product stability.

The flexible barrier material of Table One demonstrated a water vapor transmission rate of 0.61 gm/m<sup>2</sup> per day. For comparison purposes only, Saran(1 mil) has a rate of .75 gm/m<sup>2</sup> per day and polyester (1 mil) has a rate of 7.69 gm/m<sup>2</sup> per day. Thus, the flexible barrier material of the present invention has a relatively low water vapor transmission rate.

## EXAMPLE TWO

TABLE FOUR

5	ENGLISH		METRIC (SI)	
	PROPERTY	TEST	UNITS	UNITS
10	VALUE		VALUE	
	O <sub>2</sub>	ASTM	cc/m <sup>2</sup> 24hr.	cc/100in <sup>2</sup> /24hr.
	Permeation	D3985	(23 °C ,50 % RH) 4.3	0.28
15			(23 °C ,90 % RH) 4.3	0.28

The ASTM D3985 test method covers a procedure for determination of the steady-state rate of transmission of oxygen gas through plastic films. The oxygen transmission rate is defined as the quantity of oxygen gas passing through a unit area of the parallel surfaces of a plastic film per unit time under the conditions of the D3985 test method.

The first step in the oxygen gas transmission test is to equilibrate the flexible barrier material in a dry environment (relative humidity less than 1%).

The flexible barrier material is placed between two chambers at ambient atmospheric pressure. One chamber contains oxygen while the other is slowly purged by a stream of nitrogen. As oxygen gas permeates through the barrier material into the nitrogen chamber, the oxygen gas is transported to a coulometric detector where it produces an electrical current, the magnitude of which is proportional to the amount of oxygen flowing into the detector per unit time.

The flexible barrier material of Table One had an oxygen permeation of 4.3 cc/m<sup>2</sup> per 24 hour period. There is illustrated in FIG. 8 a graph of the oxygen permeation versus humidity for PET/SiOx compared to EVOH. There is illustrated in FIG. 9 a graph of oxygen permeation versus PET/MOx film.

- 5 elongation for three flexible barrier materials of the present invention. There is illustrated in FIG. 10 a graph of oxygen permeation versus temperature for PET/SiOx compared to PVDC.

## EXAMPLE THREE

5	TABLE FIVE			
	ENGLISH		METRIC (SI)	
	PROPERTY	TEST	UNITS	VALUE
10	VALUE			UNITS
	GELBO	F392	cc/m <sup>2</sup> 24hr.	cc/100in <sup>2</sup> /24hr.
15	<u>FLEX</u> :	(23 °C ,75 % RH)		
	Cycles			
	0		4.3	0.28
	25		4.7	0.30
20	50		5.3	0.34
	100		5.8	0.37
25				

ASTM test method F392 is the standard test method for the flex durability of a flexible material. This test method covers the determination of the flex resistance of flexible barrier materials. Pinhole formation is the criterion presented for measuring failure, however other tests such as gas-transmission may be used as a substitute or complement to this test. Table Five illustrates the results from an oxygen permeation test to determine the flex resistance of the flexible barrier material.

## 20

In conducting the test, the flexible barrier material is flexed at standard atmospheric conditions. The flexing conditions and number of severity of flexing strokes may vary. The flexible barrier material of Table One was subjected to cycles of 25, 50 and 100. The flexing action consists of a twisting  
5 motion followed by a horizontal motion, thus, repeatedly twisting and crushing the film. The flexing action is performed by a Gelbo Tester which is available from United States Testing Co., Inc., of Hoboken, New Jersey. The frequency is at a rate of 45 cycles per minute. Flex failure is determined by measuring the oxygen permeation according to the procedure set forth in Example Two.

10 What is quite remarkable is the continued flexibility of the flexible barrier material of the present invention, even after being subjected to 100 cycles on the Gelbo tester. As illustrated in Table Five, the oxygen permeation only increases from 4.3 cc/m<sup>2</sup> 24hr to 5.8 cc/m<sup>2</sup> 24hr after 100 cycles. There is illustrated in  
15 FIG. 7 a graph of the Gelbo Flex testing of three flexible barrier materials of the present invention. The ability to maintain its flexibility is one of the most novel properties of the present invention. This persistent flexibility enables the flexible barrier material of the present invention to be ideally utilized as a packaging material for pumpable foods. The persistent flexibility also enables the  
flexible barrier material of the present invention to withstand adverse distribution  
20 conditions and still be in an acceptable condition for the final consumer.

21

## EXAMPLE FOUR

TABLE SIX

5	ENGLISH PROPERTY VALUE	METRIC (SI)		
		UNITS	VALUE	UNITS
10	ELONGATION AT BREAK			
		MD %	160	MD % 160
15		TD %	230	TD % 230
	TENSILE	MD MPa	32	MD Kpsi 4.7
20				
	STRENGTH AT BREAK	TD MPa	28	TD Kpsi 4.1
25				
	TENSILE MODULUS	Kpsi	135	MPa 925

30 Table Six provides the results of the tensile properties under ASTM D882 for the flexible barrier material of table one. The tensile properties tested by this test provide information on the tensile modulus, the tensile energy to break and the tensile strength of the flexible barrier material. The tensile modulus of elasticity is an index of the stiffness of the plastic. The tensile energy to break is

35 the total energy absorbed per unit volume of the material up to the point of rupture.

## EXAMPLE FIVE

5	TABLE SEVEN			
	ENGLISH		METRIC (SI)	
10	PROPERTY TEST	UNITS	VALUE	UNITS
	VALUE			
	COEFFICIENT OF FRICTION	ASTM D1894	TD grams	TD grams
15	Static			
	inside/metal	0.33		0.33
	outside/metal	0.36		0.36
20	Kinetic			
	inside/metal	0.21		0.21
	outside/metal	0.19		0.19

25           ASTM D1894 covers the determination of coefficients of starting and sliding friction of plastic film when sliding over itself or other substances. The coefficient of friction is defined as the ratio of the frictional force to the force, usually gravitational, acting perpendicular to the two surfaces in contact. This

30   coefficient is a measure of the relative difficulty with which the surface of one material will slide over an adjoining surface of itself, or of another material. The static coefficient is related to the force measured to begin movement of the surfaces relative to each other. The kinetic coefficient is related to the force measured in sustaining this movement.



## EXAMPLE SIX

TABLE EIGHT

5	ENGLISH		METRIC (SI)			
	PROPERTY	TEST	UNITS	VALUE	UNITS	VALUE
10	VALUE					
	TEAR	D1922	MD grams	290	MD grams	290
	STRENGTH		TD grams	270	TD grams	270

15

ASTM D1922 covers the determination of the average force to propagate tearing through a specified length of the plastic film. The force in grams required to propagate tearing across a film is measured using a precisely calibrated pendulum device. Acting by gravity, the pendulum swings through an arc, tearing the plastic film from a precut slit. The plastic film is held on one side by the pendulum and on the other side by a stationary member. The loss in energy by the pendulum is indicated by a pointer. The scale indication is a function of the force required to tear the plastic film.

25

Table Nine sets forth the specifications for another film structure of a flexible barrier material of the present invention. The flexible barrier material is transparent, has a very high barrier property, and capable of reverse printing. The flexible barrier material may be fabricated into a self-supporting pouch. Tables ten through twelve demonstrate the novel properties of the flexible barrier material of the present invention. The synergism arising from the film structure is quite unexpected as pertaining to barrier performance. Where PET/SiOx by itself may have an oxygen permeation of 3.0 cc/m<sup>2</sup>/24hr/atm, and EVOH by itself may have an oxygen permeation of 3.0 cc/m<sup>2</sup>/24hr/atm, the combined film structure containing both PET/SiOx and EVOH has an oxygen permeation of 0.5 cc/m<sup>2</sup>/24hr/atm.

Table Nine

	<u>Layer :</u>	<u>Comment:</u>	<u>Type:</u>
5	PET	Suitable for Food Packaging Material	Biaxially Oriented PET
	SiOx	Suitable for Food Packaging Material	Plasma Enhanced Chemical Vapor Deposited SiOx
10	Printing Ink	Suitable for Food Packaging Material	Flexo , Max 8 colors Roto
15	Adhesive	Food Grade Adhesive	Adhesive for laminating LDPE film to SiOx surface Retort/Hot Fill Spec.
20	LDPE/LLDPE Food Grade LLDPE/LDPE Polymers		3.5 Mil thick blown film of blend: 75% LDPE , MFI: 0.7-0.8 25% C4 - LLDPE: MFI 0.8-1.0
	Adhesive	Food Grade Adhesive	Adhesive for laminating LDPE film to SiOx surface Retort/Hot Fill spec.
25	Barrier Layer	Food Grade	EVOH
	Adhesive	Food Grade Adhesive	Adhesive for laminating LDPE film to SiOx surface Retort/Hot Fill specification
30	LDPE/LLDPE Food Grade LLDPE/LDPE Polymers		3.5 Mil thick blown film of blend: 75% LDPE , MFI: 0.7-0.8 25% C4 - LLDPE: MFI 0.8-1.0
35			

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Table Ten

	Property	Test Method	Units	Values
5	Gauge		$\mu\text{m}$ mil	79 3.1
10	Oxygen Permeability	ASTM D-3985	cc/m <sup>2</sup> /24hr/atm.	0.5
	Dart Impact Force	ASTM D-4272	N	230
15	Puncture Force	ASTM F-1306	N	27

27

Table Eleven

## Oxygen Permeation vs. Gelbo Flexing

5	Flexes	O2 Permeation cc/m2 24hr.atm.
	0	0.5
10	100	0.5
	200	0.5
	300	0.5
15		

20

Table Twelve

## Oxygen Permeation vs. Humidity

25	RH Humidity %	O2 Permeation cc/m2 24hr.atm.
	0	0.5
30	50	0.5
	95	0.7

28

## CLAIMS

I claim as my invention the following:

- 5    1.     A transparent multilayer structure comprising:
- an exterior film selected from the group consisting of high density polyethylene, polyethylene terephthalate, polypropylene, polyethylene naphthalate and polyamide;
- a metal oxide deposition on the exterior film having a thickness
- 10   range of approximately 5 to 500 nanometers and having a formula of  $MO_x$  where  $x$  has a range of approximately 1.5 to approximately 2.5 and  $M$  is selected from the group consisting of silicon, aluminum and iron; and
- an interior film juxtaposed to the metal oxide deposition.
- 15   2.     The transparent multilayer structure according to claim 1 further comprising a barrier layer juxtaposed to the interior film and a polyolefin layer juxtaposed to the barrier layer.

20

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3. A transparent laminate for packaging of food products, the laminate comprising:

an exterior film selected from the group consisting of high density polyethylene, polyethylene terephthalate, polypropylene, polyethylene naphthalate and polyamide, the exterior film having a metal oxide deposition thereon, the metal oxide deposition having a thickness range of approximately 5 to 500 nanometers and having a formula of  $MO_x$  where x has a range of approximately 1.5 to approximately 2.5 and M is selected from the group consisting of silicon, aluminum and iron;

10 a barrier layer juxtaposed to the exterior film with the metal deposition thereon; and

a polyolefin layer juxtaposed to the barrier layer.

15

20

4. A transparent laminate for packaging of food products, the laminate comprising:

an exterior film selected from the group consisting of high density polyethylene, polyethylene terephthalate, polypropylene, polyethylene naphthalate and polyamide, the exterior film having a metal oxide deposition thereon, the metal oxide deposition having a thickness range of approximately 5 to 500 nanometers and having a formula of  $MO_x$  where x has a range of approximately 1.5 to approximately 2.5 and M is selected from the group consisting of silicon, aluminum and iron;

10 a polyolefin layer juxtaposed to the metal deposition of the exterior layer; and  
a barrier layer juxtaposed to the polyolefin layer.

5. The invention according to any of the afore-mentioned claims wherein the exterior film has a thickness range of approximately 8 to approximately 20 microns.

6. The invention according to any of the afore-mentioned claims wherein the interior film has a thickness range of approximately 25 to approximately 150 microns.



## 31

7. The invention according to any of the afore-mentioned claims wherein the interior film or the polyolefin layer is selected from the group consisting of linear low density polyethylene, ultra low density polyethylene, metallocene linear low density polyethylene, low density polyethylene, medium density polyethylene, high density polyethylene, polypropylene, copolymers of polypropylene, copolymers of ethylene vinyl acetate and mixtures thereof.

8. The invention according to any of the afore-mentioned claims wherein the M is silicon.

10

9. The invention according to any of the afore-mentioned claims wherein the exterior film is biaxially oriented polyethylene terephthalate.

10. The invention according to any of the afore-mentioned claims wherein the interior film or the polyolefin layer is a blend of linear low density polyethylene and low density polyethylene.

15

11. The invention according to any of the afore-mentioned claims wherein the polyolefin layer has a thickness range of 5 to 50 microns.

20

12. The invention according to any of the afore-mentioned claims wherein the barrier layer is EVOH or a blend of EVOH and another polymer material.

25

13. A process for fabricating a transparent multilayer structure, the process comprising the steps of :

providing an exterior film selected from the group consisting of high density polyethylene, polyethylene terephthalate, polypropylene,

5 polyethylene naphthalate and polyamide, with a metal oxide deposition on the exterior film to form a deposited exterior film, the metal oxide deposition having a thickness range of approximately 50 to approximately 500 nanometers and having a formula of  $MO_x$  where x has a range of approximately 1.5 to approximately 2.5 and M is selected from the group consisting of silicon,  
10 aluminum and iron; and

laminating a second film to the deposited exterior film.

14. The process according to claim 13 wherein the second film has an interior film, a barrier layer and a polyolefin layer according to any of the afore-  
15 mentioned claims.

15. The invention according to any of the afore-mentioned claims wherein the  
20 exterior film is also a print layer.

## 33

16. A self-supporting transparent container for flowable materials fabricated from a transparent multilayer film or transparent laminate of any of the aforementioned claims, the self-supporting transparent container comprising a flexible gusseted panel secured to a marginal portion of a plurality of side walls of the container and folded inwardly therebetween.
17. The self-supporting transparent container according to claim 16 further comprising a transverse seal having an unsealed area of a predetermined configuration.
18. The self-supporting transparent container according to claim 16 wherein the transverse seal has a tear notch for exposing the unsealed area while partially maintaining the transverse seal, the exposed unsealed area permitting the placement of an insertion for removing the contents of the self-supporting transparent container, the insertion corresponding in shape to the predetermined configuration of the unsealed area.
19. The self-supporting transparent container according to claim 18 wherein the straw insertion has an elongated body with an aperture therethrough, the elongate body further comprising an insert portion for penetration to the contents, a spout portion for dispensing a contents of the container, the spout portion disposed above the insert portion, and a knob disposed above the spout portion, the knob disengageable from the spout portion, the knob configured for placement within the spout portion to prevent leakage of the contents through the insert.

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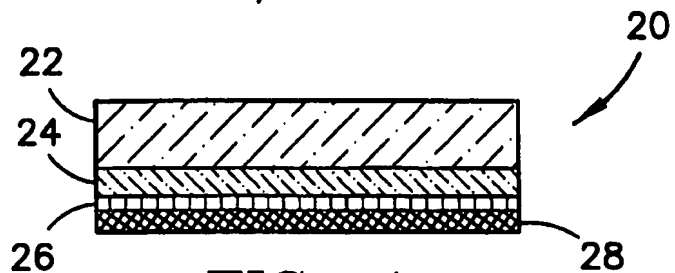


FIG. 1

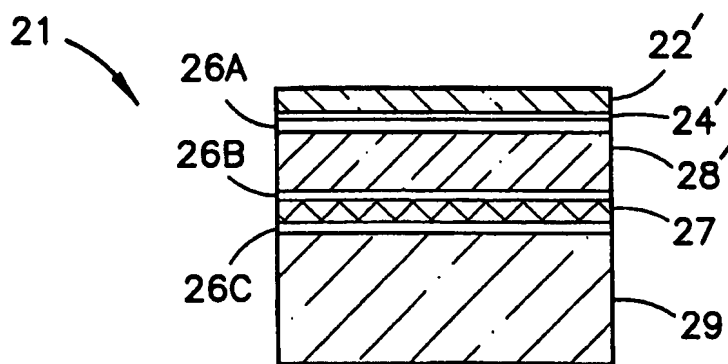


FIG. 1A

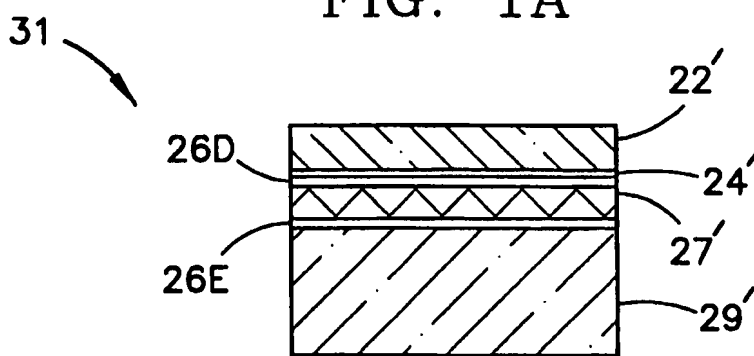


FIG. 1B

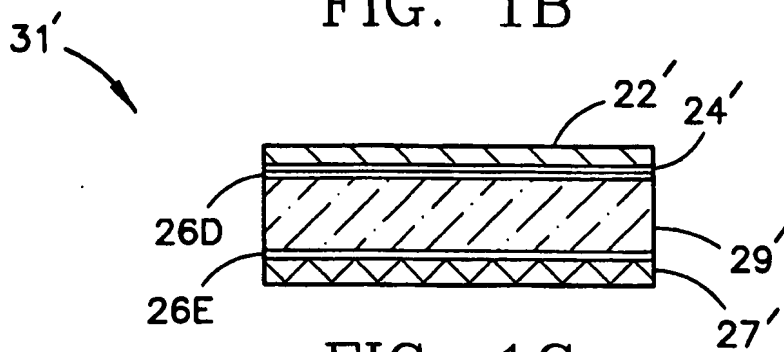


FIG. 1C

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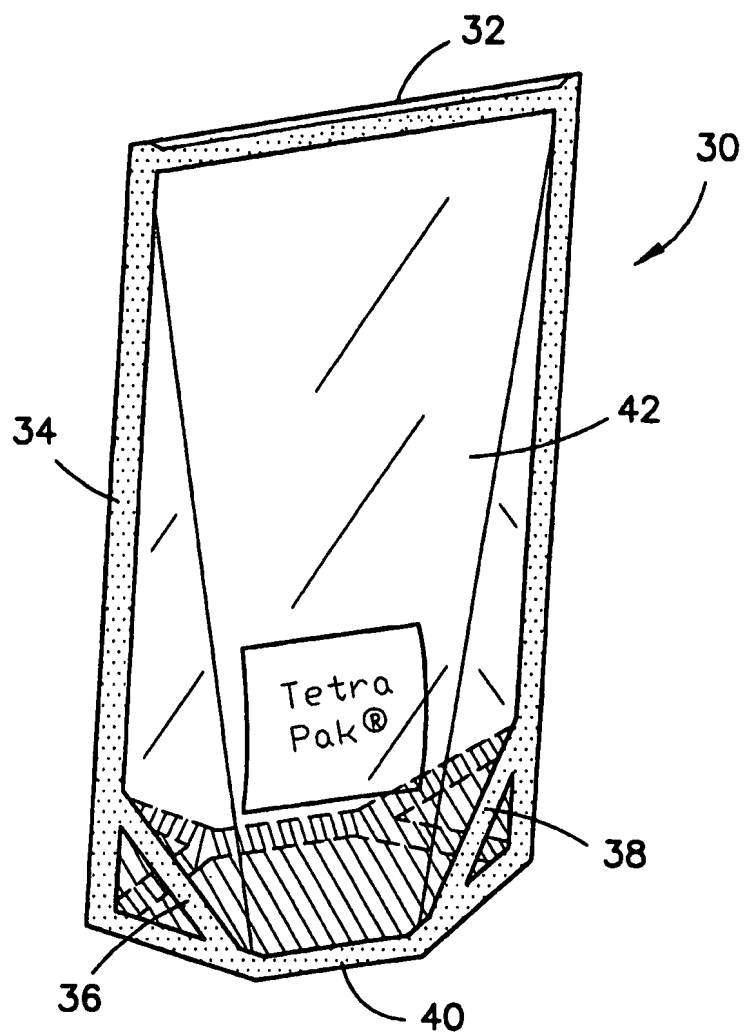


FIG. 2

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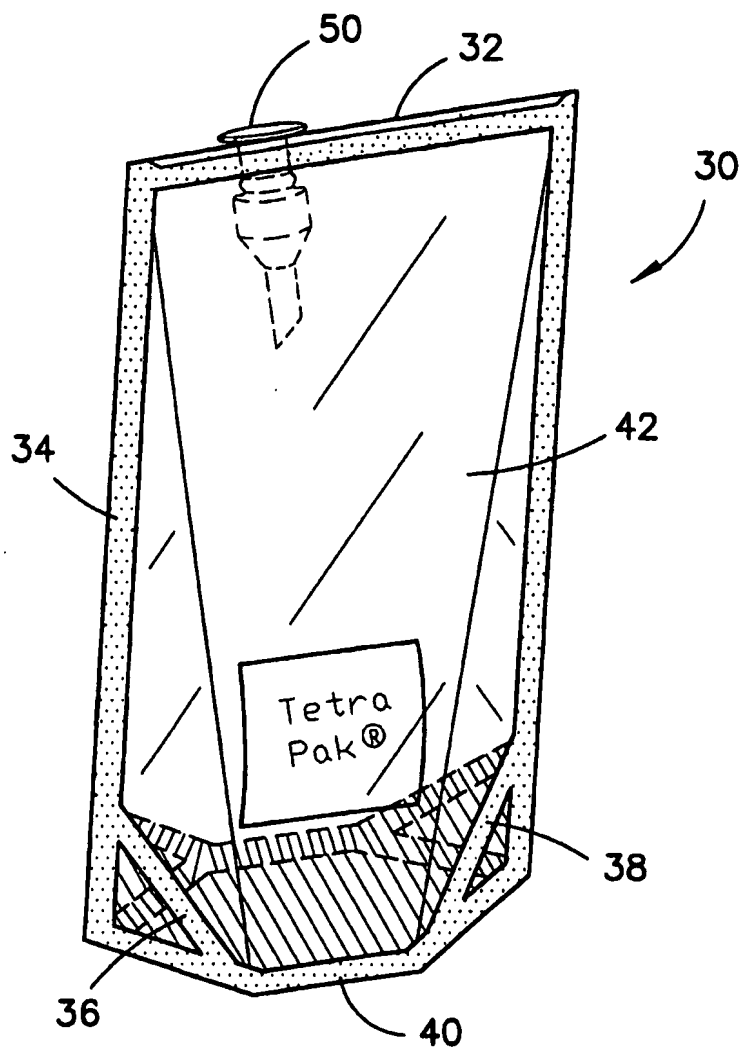


FIG. 3

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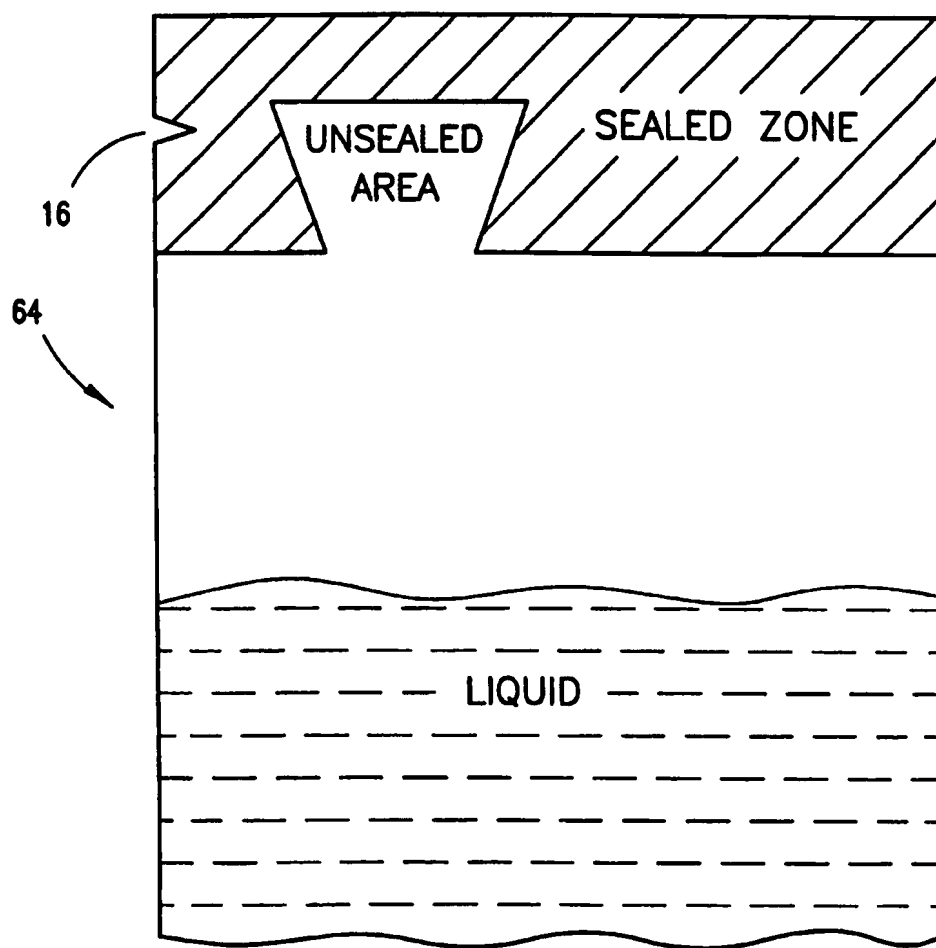


FIG. 4

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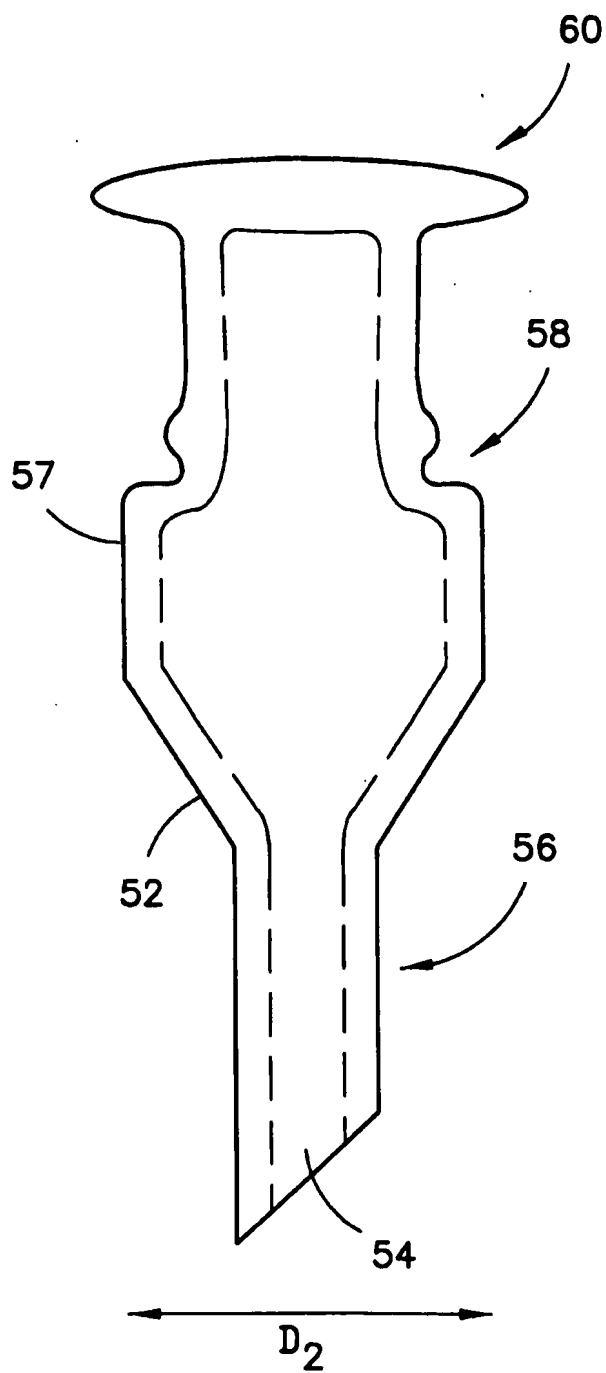


FIG. 5



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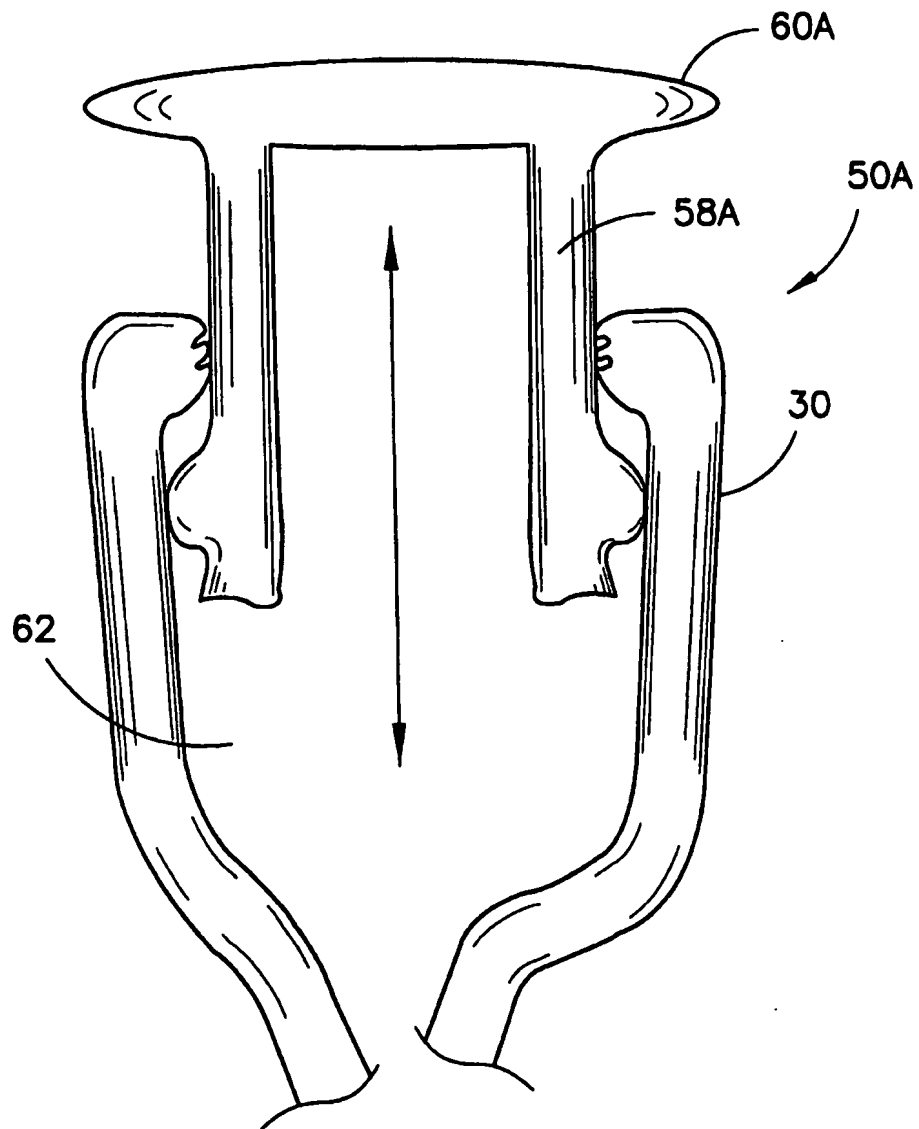


FIG. 6

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# GelboFlexed PET/SiOx-O2Permeation

cc O2/m2 24hr atm at 23° C

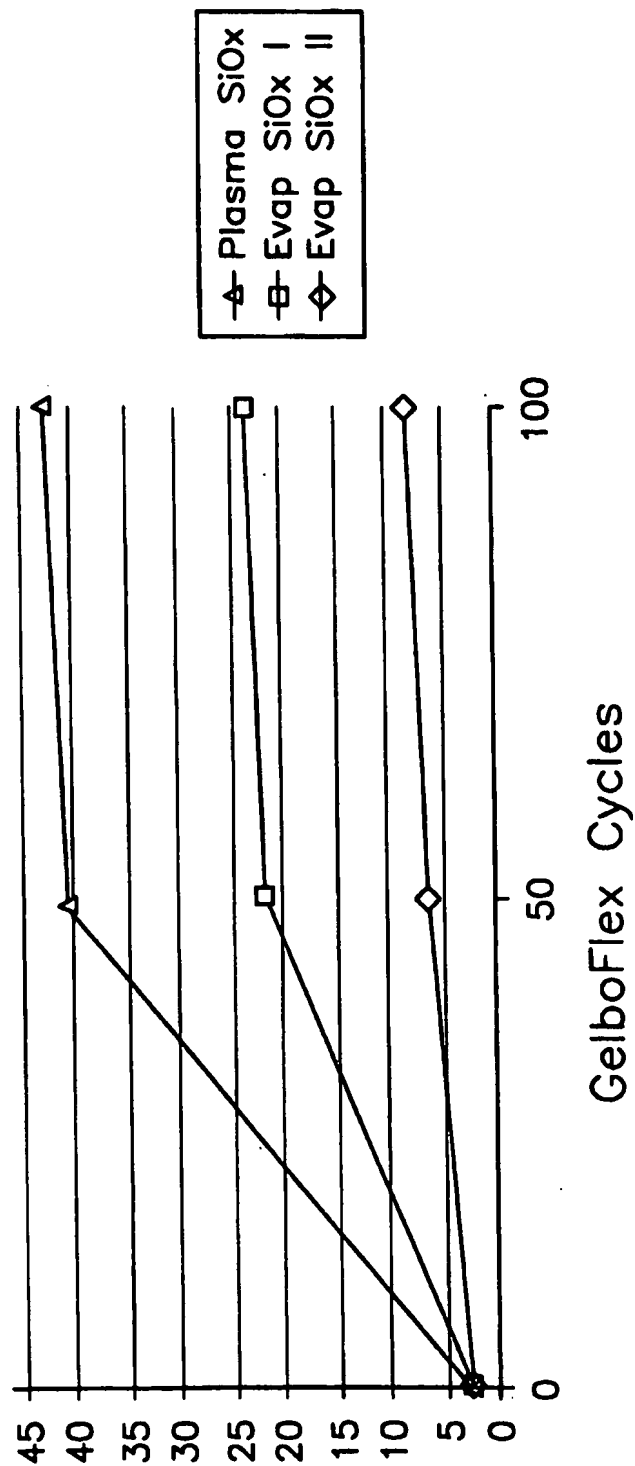


FIG. 7

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# O<sub>2</sub> Permeation vs Humidity

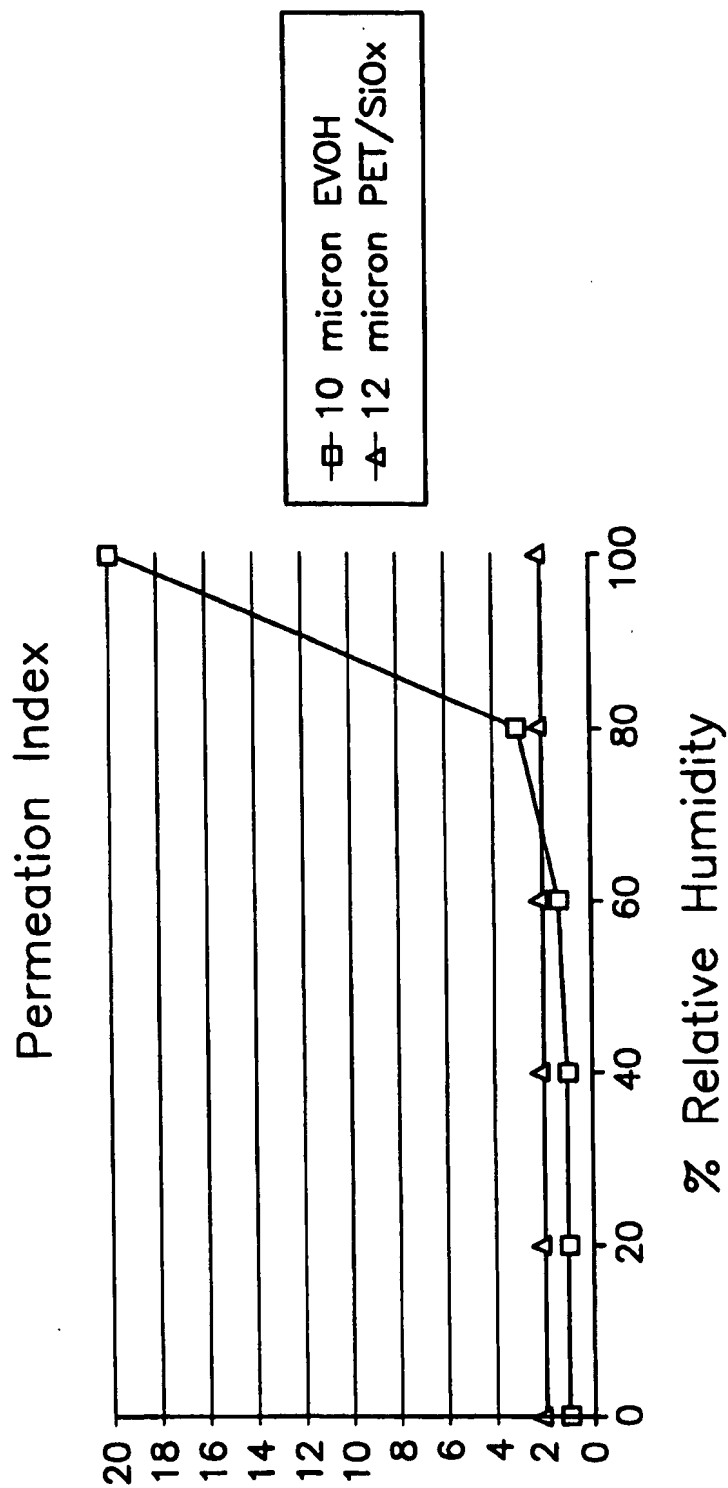


FIG. 8

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# O<sub>2</sub> Permeation vs PET/SiO<sub>2</sub> Film Elongation

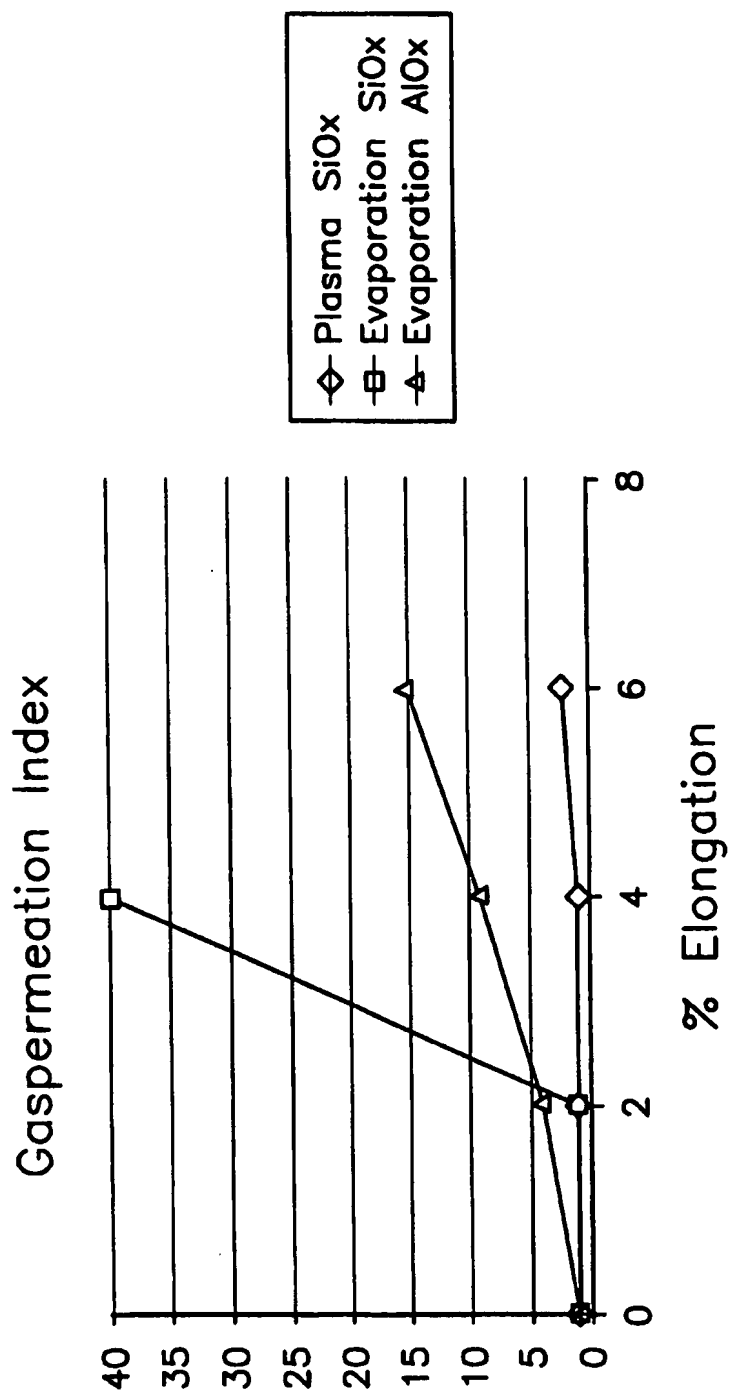


FIG. 9

10/10

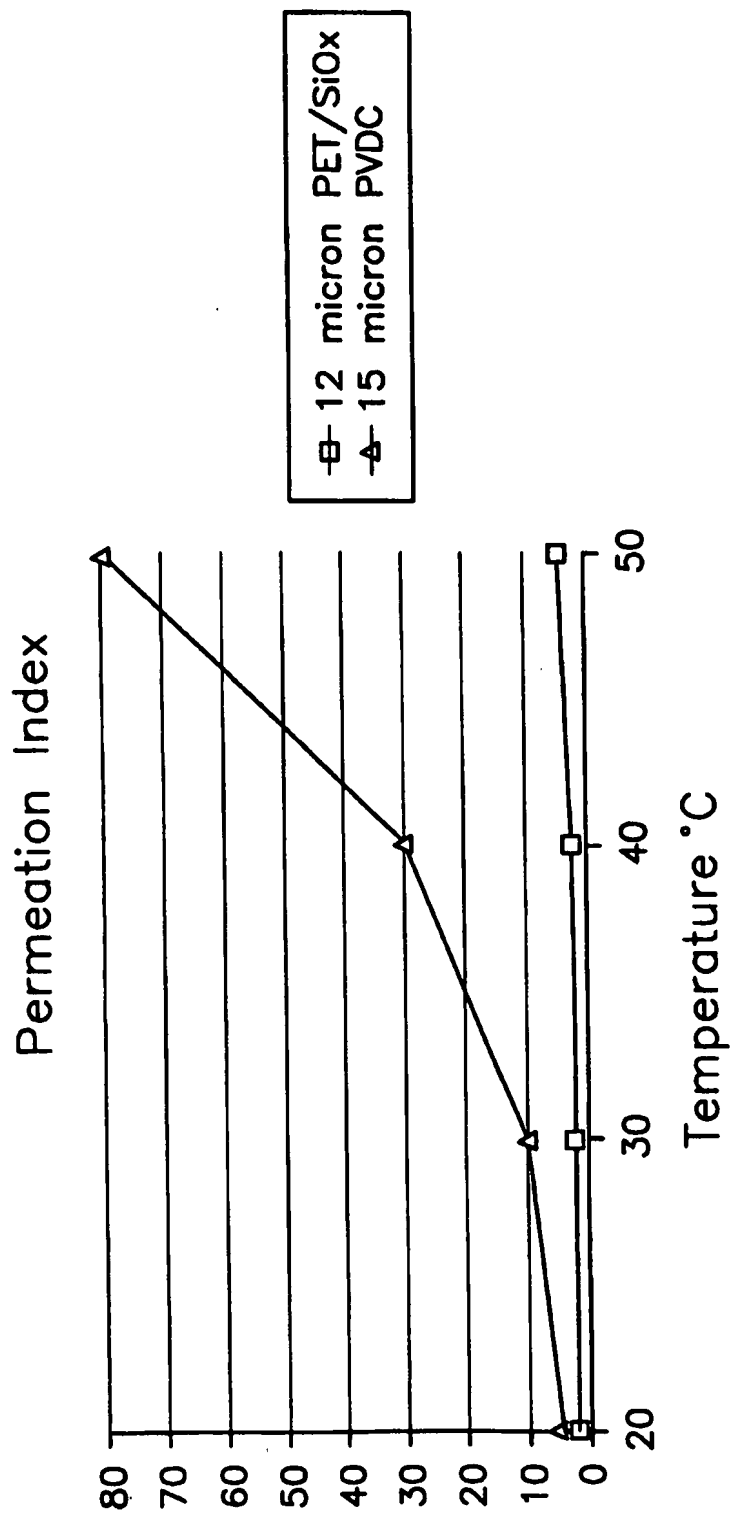
O<sub>2</sub> Permeation vs Temperature

FIG. 10